STUDY ON FORMATION / DISSOCIATION MECHANISM OF GAS HYDRATES AND RECOVERY OF PURE HYDRATE CRYSTAL USING HIGH PRESSURE CRYSTALLIZATION TECHNIQUE

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INTRODUCTION

Gas hydrate is the species that guest molecules (CO_2, CH_4 etc.) are included in the cage of hydrogen-bonding network of water molecules. Recently, it was found that there are great quantity of methane hydrate in the sediment below the sea bottom. Since Japan has no natural energy resources, we pay much attention to the natural gas hydrates as one of the hopeful energy source for the future. To establish elemental technologies for mining methane hydrate, we started fundamental and also practical study of gas hydrate.

The observation of real crystallization process is indispensable to study formation / dissociation mechanism precisely. On the other hand, it is important for establish methane hydrate recovering method to get pure hydrate crystals and measure accurate physical and chemical property of them.

To achieve these objects, we are constructing high pressure crystallization apparatus with optical window. In this presentation, we will report the resent result of hydrate crystal formation and recovery experiment with this apparatus.

As a fundamental research on the gas hydrate formation, we are interested in molecular clustering structure of aqueous solution. As for the interaction of magic numbered water cluster, $H^+(H_2O)_{21}$, which has dodecahedral structure, with organic molecules, it was observed that tetrahydrofuran (THF) did not dissociate the hydrogen-bonding network of $H^+(H_2O)_{21}$ cluster; however, methanol dissociated it. In the mass spectra of clusters generated from THF-water and methanol-water mixtures, $H^+(H_2O)_{21}$ clusters contact with THF, $H^+(H_2O)_{21}(THF)_n$:n=1,2,3..., and $H^+(H_2O)_{21}$ clusters substituted by methanol, $H^+(H_2O)_{21-n}(CH3OH)_n$: n=1,2,3..., were observed, respectively[1]. Such molecular structures in aqueous solutions seem to be related with the nucleation mechanism of hydrate. That is, THF makes hydrates, but methanol works as gas hydrate inhibitor. We also intend to carry out methane hydrate formation experiment with any additives such as THF or CH_3OH,etc., and discuss nucleation mechanism of gas hydrate with the clustering structure of water molecules which were observed by cluster beam mass spectrometer.

EXPERIMENTAL

High pressure crystallization apparatus with optical vessel

Fig.1 shows the schematic diagram of the high pressure crystallization apparatus with optical vessel. Photographs of this apparatus and main vessel are also shown in Fig.2 and Fig.3 respectively. As shown in Fig.1, main vessel (C1) and sub vessel (C2) are piston-cylinder type high pressure vessels. Inner diameter and volume of these vessels are 15 mm and 20 mℓ respectively. The main vessel has a pair of sapphire windows to observe crystallization process on both side and stainless filter to separate liquid phase from solid phase on the bottom. Main vessel is soaked in a silicon oil bath[Temperature control range ; -30℃～+130℃]. This oil bath also has optical windows and crystallization process can be observed through these windows with microscope or multi channel spectrophotometer. Compression of vessels is carried out by using oil pressure equipment (19). Main vessel is connected with gas supplying system, which can supply host gases continuously under high pressure(max. under 400kg/cm^2). Control of gas flow rate is carried out by flow controller for high flow rate (3) [0.5～5N ℓ/min] and low flow rate (4) [0.01～0.1N ℓ/min]. Maximum pressure of crystallization unit is 4000kg/cm^2.

Crystallization and separation procedure

Sample mixtures (pure water and THF, pure water and CH_4 etc.) are injected into the main vessel (**C1**) and compressed to form hydrate crystals. The excess liquid phase is removed from the crystals in the main vessel (**C1**) to the sub vessel (**C2**), keeping the pressure in the main vessel constant and slightly decreasing the pressure in the sub vessel. After separation process is finished, stop valve between two vessels (**VH1**) is shut and crystals are recovered.

To confirm performance of the apparatus, crystallization and separation of pure indole from indole/isoquinoline mixture was carried out. Then, we started hydrate formation experiment of THF/water system and CH_4/water system. In case of methane/water system, to prevent dissociation of methane hydrate, the main vessel is cooled to about 80℃ by dry ice/methanol bath before the decreasing of main vessel pressure and taking out of hydrate crystal.

RESULT AND DISCUSSION

Formation and separation of high purity indole crystal by high pressure crystallization method

Fig.4 shows the typical operation diagram of high pressure crystallization. Sample solution is indole-isoquinoline mixture (80mol%-indole). Separation process is as follows.

1) Inject sample mixture into main vessel (**C1**) and compressed to 1000kg/cm^2 step wise under 50 ℃. In this process, pure indole crystal is formed and impurities concentrated into liquid phase

2) Hold the pressure of main vessel at 1000kg/cm^2 until solid-liquid phase equilibrium is achieved.

3) Open the stop bulb (**VH1**) between main and sub vessel and remove liquid phase from the crystal. In this process, pressure in the main vessel is constant (1000kg/cm^2) all the way. However, as sown in Fig.4, after almost stop the piston displacement, the pressure which is indicated in pressure gauge (**PH1**) gradually decreased and finally reach almost atmospheric pressure. This means that almost all the liquid is removed and pressure in the main vessel can not transmitted to pressure gauge (**PH1**). At that time, crystal in main vessel is squeezed under 1000kg/cm^2 and remained liquid is perfectly separated.

4) Pressure of main vessel is decreased to atmospheric pressure and separated crystal is recovered.

The purity of recovered solid was measured by gas chromatography. Indole concentration of that crystal was 98mol% and it was known that high purity crystal can be separated by this high pressure crystallization apparatus.

Formation and separation of THF hydrate and methane hydrate

Generally, autoclave type high pressure vessels were used for hydrate formation experiment and it is said that stirring of the vessel is important to form hydrate crystal. However, it is difficult to stir sample in main vessel (**C1**) in our apparatus. As mechanical stirring is not performed at natural hydrate formation process, stirring seems to be not always necessary. To confirm if methane hydrate formation is occurred without stirring or not, we slowly injected methane gas into an autoclave type optical vessel which is filled with pure water. (details will be described in another presentation of our group in this meeting by Dr.Komai.) As a result, film like hydrate crystal was formed almost instantly with rising of methane gas babble under the condition of 2℃、100kg/cm^2. Though it seemed to need fairly long time to make methane gas included in the hydrate film into crystal perfectly, it was confirmed that nucleation of hydrate can be occurred without mechanical stirring. According to this result, we tried hydrate formation experiment with the high pressure crystallization apparatus.

First, THF/water (THF : H_2O = 1 : 25 molar ratio) mixture was injected into the apparatus and examined efficiency of hydrate formation and separation. Temperature and separation pressure are 4℃ and 200kg/cm^2. After separation of excess water, main vessel was cooled to -10℃ and THF hydrate was recovered. From the pressure which is indicated on pressure gauge (PH1), we confirmed that hydrate and excess water was perfectly separated as same as indole-isoquinoline mixture. Photograph of recovered THF hydrate is shown in Fig.5.

Next, methane hydrate formation and separation experiment was performed with this apparatus. 6mℓ of pure water and 4 mℓ of methane gas was injected into main vessel1, and hydrate was formed under

4℃,400kg/cm^2. After separation of methane hydrate from water phase was finished, hydrate crystal was cooled to about -80℃ by methanol/dry ice bath. (Under -80℃, the dissociation pressure of methane hydrate become lower than atmospheric pressure.) Then, pressure of main vessel was decreased to atmospheric pressure and formed crystal was recovered. Photograph of recovered solid is shown in Fig.6. Recovered crystal is flammable white solid and dissolve with discharging babbles. Though It thought to be a methane hydrate, detailed analyses was still not performed and purity of crystal is not confirmed for the moment.

CONCLUSION

We constructed the gas hydrate formation/separation apparatus using high pressure crystallization method and confirmed a formation and recovery of gas hydrate by this equipment. For the present, adjustment of gas supplying unit was not finished perfectly and strict control of crystal formation is not achieved. Also, the system for observation of hydrate crystal formation is under adjustment.

From now on, we try to improve high pressure mass controller in gas supplying unit and structure of optical system and establish the technique for formation of pure hydrate and recover it. With the separated gas hydrate, we are going to measure physical and chemical property of it precisely.

We are also carrying out methane hydrate formation experiment with THF or CH_3OH. we will also make a discussion about influence of these additives to methane hydrate formation with the comparison of the clustering structure of water molecules which was observed by cluster beam mass spectrometer.

ACKNOWLEDGEMENT

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1: Pressure gauge 2: Flow meter
3: Flow controller for high flow rate
4: Flow controller for low flow rate
5: Stroke gauge 6: Thermocouple
7: Pressure gauge 8: Vacuum pump
9: Sampling tube 10: Relief valve
11: High pressure gas buster
12: Pressure control valve
13:Constant temperature oil bath
14: Optical window 15: Monitor
16: Video recorder
17: C.C.D camera 18: Microscope
19: Oil pressure equipment
20: halogen lump

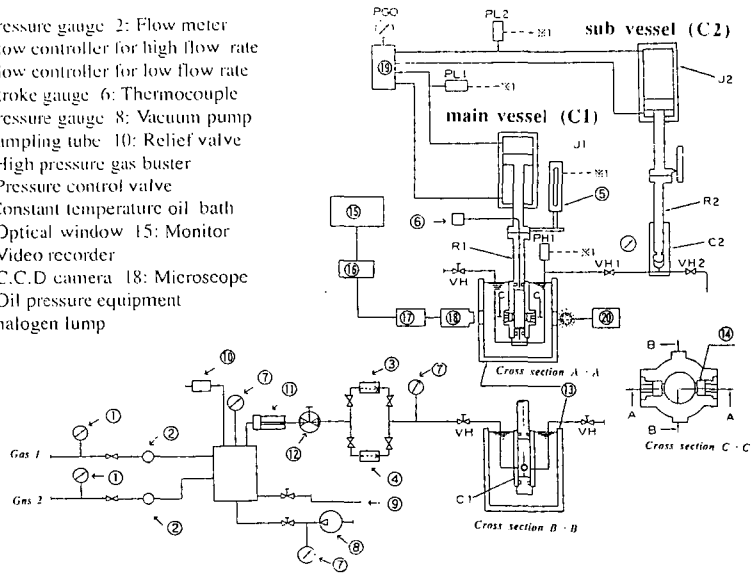

Fig.1 Schematic diagram of the high pressure crystallization apparatus with optical vessel

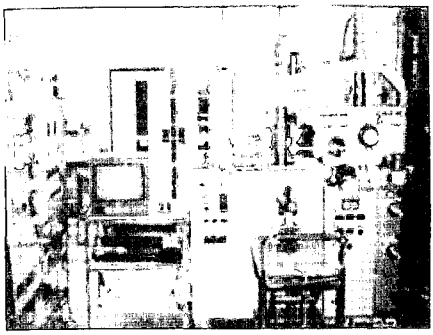

Fig.2 Photograph of the high pressure crystallization apparatus.

Fig.3 Photograph of the main vessel (C1)

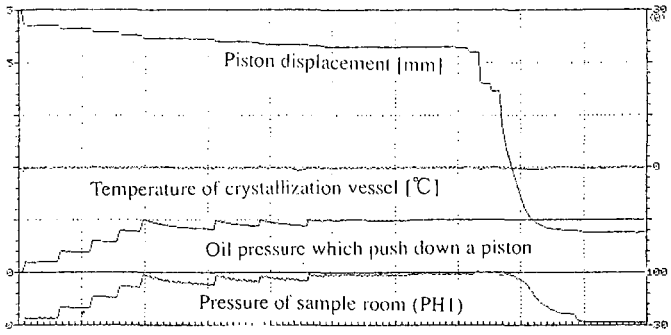

Fig.4 Operation diagram of crystallization and separation of pure indole from indole/isoquinoline mixture using high pressure crystallization technique (Indole concentration is 80mol%, separation temperature = 50℃, separation pressure = 1000kg/cm^2)

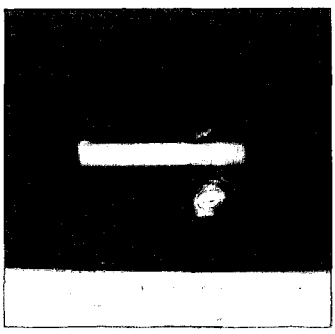

Fig.5 Photograph of recovered THF hydrate (separation temperature=1℃, separation pressure=200kg/cm^2)

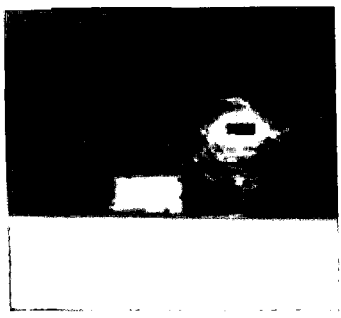

Fig.6 Photograph of recovered CH_4 hydrate (separation temperature=4℃, separation pressure=400kg/cm^2)